



Office Reference: UMJ-102-B (UM-1544p1)

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE  
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

Applicant: Curtis L. Munson and Ralph T. Yang  
Serial Number: 09/632,891  
Filing Date: August 7, 2000  
Examiner/Art Group Unit: Tam M. Nguyen/1764  
Title: SULFUR RESISTANT ADSORBENTS

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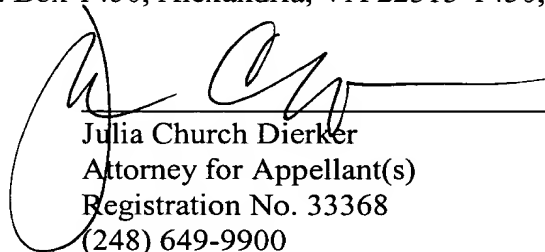
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APPEAL BRIEF

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Sir:

Please enter the following Appeal Brief in the appeal filed December 23, 2003.

REAL PARTY IN INTEREST

The Assignees, the Regents of the University of Michigan and Chevron U.S.A., are the real parties in interest.

RELATED APPEALS AND INTERFERENCES

A Notice of Appeal was filed in the above-identified application on July 8, 2002. A Brief in Support of that Appeal was timely filed on September 9, 2002. Per the Examiner's request, a revised Appeal Brief was filed on November 25, 2002. In light of that revised Appeal Brief, the Examiner re-opened prosecution of the subject case in a non-final Office Action dated February 19, 2003.

STATUS OF CLAIMS

Claims 1-10, 15-25, 27-29, 31, 32, 34-54 and 65-68 are pending and are attached as the Appendix. No claim is allowed.

### STATUS OF AMENDMENTS

No Amendment under Rule 37 C.F.R. § 1.116 was filed in response to the final Office Action of August 26, 2003.

### INTRODUCTION

Appellants believe that an important argument has not been adequately and fully considered by the Examiner during prosecution of the above-identified application. In his "Response to Arguments," the Examiner asserts that it would be expected that the adsorbents described in U.S. Patent No. 6,215,037; U.S. Patent No. 6,426,881; and Padin (the propriety of the citation of Padin will be discussed hereinbelow) would be effective in separating hydrocarbons in the presence of the claimed amount of hydrogen sulfide because the adsorbents are the same as the "*claimed adsorbent*." (emphasis added) Appellants respectfully submit that the subject invention as defined in the pending claims is a **method**. Appellants have unexpectedly and fortuitously discovered a new use for sorbents described in '037, '881 and Padin—this new use is proper subject matter for method claims. Since there was no teaching or suggestion in '037, '881 or Padin of the method of the present invention as defined in the pending claims, the Examiner's assertion is irrelevant that the sorbents recited as part of the method claims may be described in '037, '881, or Padin.

### SUMMARY OF THE INVENTION

The present invention relates generally to a method for selectively separating olefins from paraffins when such olefins and paraffins are part of a gaseous mixture including hydrogen sulfide, the hydrogen sulfide present in amounts normally present in conventional cracked gas streams (Page 13, lines 12-22). Adsorbents useful in the present method are resistant to and/or tolerant of hydrogen sulfide poisoning (Page 1, lines 11-17).

The presence of sulfur compounds is generally known to have deleterious effects in various petroleum refining processes. For example, in catalytic reforming, the catalyst used is often platinum supported on high-purity alumina. However, the platinum on the catalyst is seriously deactivated by sulfur compounds, and therefore the feedstock is desulfurized to less than 3 ppm by weight of sulfur before the reforming. See, for example, Tedder, J.M., A. Nechvatal and A.H. Jubb, Basic Organic Chemistry, Part 5: Industrial Products, Chapter 3.2, "Preparation of Primary Petrochemicals: Reforming," pp. 53-60 (1975). (Page 3, lines 3-14)

U.S. Patent No. 6,063,723 issued to Miller also demonstrates that sulfur is known to have deleterious effects. The '723 patent discloses a sulfur tolerant zeolite catalyst for use in catalytic dehydrogenation of light paraffinic hydrocarbons. This catalyst is prepared such that it has a very specific alkali to aluminum ratio in the zeolite. Although this patent's disclosed sulfur tolerance is better than that of previously known catalysts, it is still only disclosed to be tolerant of sulfur in the range of up to 2 ppm sulfur, and more preferably up to 0.5 ppm sulfur. (Page 3, lines 15-25)

Cracked gas streams include a blend of many components, including olefins, paraffins, H<sub>2</sub>, H<sub>2</sub>S, etc. The cracked gas streams are first subjected to caustic scrubbing in order to remove hydrogen sulfide. Then, it is necessary to separate olefins from paraffins in these streams in order to obtain a product rating. Conventional methods for such separation include multiple distillation runs, one of which removes, for example, H<sub>2</sub> and methane. Thereafter, the stream includes C<sub>2</sub>'s and higher, mixed with olefins and paraffins. This stream is then distilled to separate the olefins from the paraffins. However, this distillation is very energy intensive and difficult to accomplish because of relatively close volatilities when alkene\alkane (olefin\paraffin) separation is required. For example, ethane\ethylene separation is carried out at about -25°C and 320 psig (2.603 MPa) in a column containing over 100 trays, and propane\propylene separation is performed by an equally energy-intensive distillation at about 38°C and 260 psig (1.8 MPa). It is evident that high capital costs and high operational costs are incurred in any cryogenic distillation approach. (Page 3, line 26 – Page 4, line 10)

Further, it is also very difficult to separate a diene from a mixture, particularly one containing mono-olefin. Purifying the mono-olefin, 1-butene, is particularly troublesome due to the closeness of its boiling point to that of 1,3-butadiene. In order to increase the purity of 1-butene, it is necessary to separate it from other hydrocarbons. Ordinarily, fractionation alone is cost prohibitive for completely separating 1,3-butadiene to achieve the desired purity of 1-butene in these mixtures. Presently, butadiene is separated from olefins and paraffins primarily by distillation with selective solvents and by absorption using solutions of absorbents. Extractive distillation is relatively energy-intensive, complex and not economical. There are several drawbacks, in that this puts water vapor and/or solvent vapor into the regenerated product. Further, metal salts often are instable in solution and will precipitate out of solution. Selective absorption with metal salt solution involves additional stages with recycling of streams between stages to remove water vapor and/or solvent vapor from the regenerated product. This method has the disadvantage of being energy-intensive and requiring handling and recirculating of solvent streams which themselves contain

contaminants or are subject to degradation. Current processes for olefin\paraffin separation have not been sufficiently selective to economically achieve the desired result for purifying mixtures of unsaturated hydrocarbons. (Page 4, line 11 – Page 5, line 2)

Thus, it is an object of the present invention to provide a method which would cost-effectively and successfully achieve separation of olefins from paraffins in the presence of hydrogen sulfide. Still further, it is an object of the present invention to provide adsorbents useful in such method which are advantageously resistant to and/or tolerant of sulfur poisoning. (Page 5, lines 3 - 12)

A method of separating gaseous alkene selected from the group consisting of ethylene, propylene and mixtures thereof, from a gaseous mixture including the alkene and hydrogen sulfide, the hydrogen sulfide present in amounts normally present in conventional cracked gas streams, comprises the steps of:

contacting the gaseous mixture with an adsorbent which preferentially adsorbs the alkene, at a selected temperature and pressure, thereby producing a non-adsorbed component and an alkene-rich adsorbed component; the adsorbent comprising a carrier having a surface area, the carrier having a monolayer of a silver compound dispersed on substantially the entire surface area, the silver compound releasably retaining the alkene; and the carrier comprising a plurality of pores having a pore size greater than the effective molecular diameter of the alkene; and

changing at least one of the pressure and temperature to thereby release the alkene-rich component from the adsorbent;

wherein the adsorbent substantially maintains its adsorbent capacity and preference for the alkene in the presence of the hydrogen sulfide. (Page 13, lines 12-22; Page 8, line 6; Page 8, line 17 - Page 9, line 24)

A method for separating a diene from a mixture including the diene and hydrogen sulfide, the hydrogen sulfide present in amounts normally present in conventional cracked gas streams, comprises the step of:

contacting the mixture with an adsorbent which preferentially adsorbs the diene, at a selected temperature and pressure, thereby producing a non-adsorbed component and a diene-rich adsorbed component, wherein the adsorbent comprises an ion-exchanged zeolite selected from the group consisting of zeolite X, zeolite Y, zeolite LSX, and mixtures thereof, the zeolite having exchangeable cationic sites, and a majority of the sites having silver cation or copper cation present, and wherein the preferential adsorption occurs by  $\pi$ -complexation, and further wherein the adsorbent substantially maintains its adsorbent capacity and preference for the diene in the presence of the hydrogen sulfide. (Page 11, lines 1-17; Page 13, lines 12-22)

### ISSUES ON APPEAL

1. Whether Padin, J. and R. T. Yang, "New Sorbents for Olefin/Paraffin Separations by Adsorption via  $\pi$ -Complexation: (I) Synthesis and Effects of Anions and Substrates," Chem. Eng. Sci., Vol. 55, p. 2607-2616 (2000) (Padin) is available as a § 103 reference against claims 1-10, 29 and 65 when the subject application was filed in the U.S. Patent Office less than one year after Padin's publication date?
2. Whether the reference identified as "New Sorbents for Olefin/Paraffin Separations by Adsorption via  $\pi$ -Complexation," R.T. Yang and E.S. Kikkinides, AIChE Journal, Vol. 41, No. 3, pp. 509-517 (March 1995) complies with 37 C.F.R. 1.98(a)(2) which requires a legible copy of the reference cited, when it was legible enough for the Examiner to review and initial its citation on the Form PTO-1449 on April 16, 2001; and the Examiner cited it against pending claims in Office Actions dated April 24, 2001, October 18, 2001 and April 8, 2002?
3. Whether claims 1-10, 27-29, 32 and 65 are patentable over Padin, J. and R. T. Yang, "New Sorbents for Olefin/Paraffin Separations by Adsorption via  $\pi$ -Complexation: (I) Synthesis and Effects of Anions and Substrates," Chem. Eng. Sci., Vol. 55, p. 2607-2616 (2000) (Padin) in view of Ogawa U.S. Patent No. 6,042,797, or further in view of Ramachandran et al., U.S. Patent No. 5,744,687 ('687) under 35 U.S.C. § 103(a); or alternately over Milton U.S. Patent No. 2,882,243 under 35 U.S.C. § 103(b), when none of the references teach or suggest a method effective for use in the presence of hydrogen sulfide, the hydrogen sulfide present in amounts normally present in conventional cracked gas streams?
4. Whether claim 10 is patentable over Padin, J. and R. T. Yang, "New Sorbents for Olefin/Paraffin Separations by Adsorption via  $\pi$ -Complexation: (I) Synthesis and Effects of Anions and Substrates," Chem. Eng. Sci., Vol. 55, p. 2607-2616 (2000) (Padin) in view of Ogawa U.S. Patent No. 6,042,797, when Ogawa teaches away from a method utilizing  $\pi$ -complexation, and there is no suggestion or motivation to combine Ogawa with Padin?
5. Whether claims 65-68 are patentable over Padin, J. and R. T. Yang, "New Sorbents for Olefin/Paraffin Separations by Adsorption via  $\pi$ -Complexation: (I) Synthesis and Effects of Anions and Substrates," Chem. Eng. Sci.,

Vol. 55, p. 2607-2616 (2000) (Padin) in view of Ogawa U.S. Patent No. 6,042,797, when none of the references teach or suggest a method wherein the gaseous mixture is contained in a conventional cracked gas stream before any desulfurizing distillation steps occur?

6. Whether claims 15-25, 27, 28, 31, 32, 34-54 and 66-68 are patentably distinct from claims 1-26 of U.S. Patent No. 6,215,037, when the reference does not teach or suggest a method for separating a diene from a mixture including the diene and hydrogen sulfide, the hydrogen sulfide present in amounts normally present in conventional cracked gas streams?

7. Whether claims 1-10, 29 and 65 are patentably distinct from claims 1-19 of U.S. Patent No. 6,426,881 when the reference does not teach or suggest a method of separating gaseous alkene selected from the group consisting of ethylene, propylene and mixtures thereof, from a gaseous mixture including the alkene and hydrogen sulfide, the hydrogen sulfide present in amounts normally present in conventional cracked gas streams?

#### GROUPING OF CLAIMS

Claims 1-10, 15-25, 27-29, 31, 32, 34-54 and 65-68 stand together. Claims 1-10, 27-29, 32 and 65 are separately patentable from any other claim. Claim 10 is separately patentable from any other claim. Claims 65-68 are separately patentable from any other claim. Claims 15-25, 27, 28, 31, 32, 34-54 and 66-68 are separately patentable from any other claim. Claims 1-10, 29 and 65 are separately patentable from any other claim.

The specific reasons for the separate patentability of each group of claims is set forth in the argument section of this Appeal Brief.

#### ARGUMENT

##### The Examiner's Rejection

Claims 1-7, 10, 29 and 65 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Padin, J. and R. T. Yang, "New Sorbents for Olefin/Paraffin Separations by Adsorption via  $\pi$ -Complexation: (I) Synthesis and Effects of Anions and Substrates," Chem. Eng. Sci., Vol. 55, pp. 2607-2616 (2000) (Padin) in view of Ogawa U.S. Patent No. 6,042,797.

The Examiner states that Padin discloses a process for separating olefins (e.g. propylene) from an olefin/paraffin mixture by using an adsorbent having a monolayer of a silver compound (e.g.  $\text{AgNO}_3$ ,  $\text{AgI}$  or  $\text{AgCl}$ ) dispersed on substantially the surface area of a carrier (e.g.  $\text{SiO}_2$ ). The carrier has a BET surface area of about 384  $\text{m}^2/\text{g}$  and a pore size of about 8.4 Angstroms. The Examiner points out that the adsorption step is operated at a temperature of about 25°C and at a pressure of about 1 atm and wherein the retaining of alkene is accomplished by formation of  $\pi$ -complexation bonds between the silver compound and the alkene. The Examiner recognizes that Padin does not disclose that the gaseous alkene comprises a hydrogen sulfide in amounts normally in conventional cracked gas stream or up to 66 mole%. However, he stated that the adsorbent of Padin is the same as the claimed adsorbent and that Ogawa discloses a process for removing ethylene from a gas mixture containing ethylene and a sulfur compound (e.g., sulfur oxide) by contacting the gas mixture with an adsorbent which comprises a silver compound (silver nitrate) and zeolite. The Examiner concludes that it would have been obvious to modify the process of Padin by using an olefinic feed comprising hydrogen sulfide because sulfur compounds would not affect the outcome of the process. He states that it would be expected that the Padin adsorbent would be effective in the separation step in the presence of hydrogen sulfide in the amount of at least 0.01 mole %.

The Examiner further notes that Padin does not disclose the step of changing the pressure and/or temperature to release the alkene-rich component from the adsorbent. He goes on to state that Ogawa teaches that the adsorption step is operated at a higher temperature than the desorbing temperature. The Examiner concludes that it would have been obvious to have modified the process of Padin by changing the temperature as taught by Ogawa because such a temperature change is effective to desorb the alkene from the adsorbent.

Regarding claim 65, the Examiner notes that Padin does not disclose that the alkene feedstock is a conventional cracked gas stream before any desulfurization distillation steps. However, he concludes that it would have been obvious to modify the process of Padin by using the claimed feedstock because of the similarity between the claimed feedstock and the modified Padin feedstock.



Claims 8 and 9 are rejected under 35 U.S.C. 103(a) as being unpatentable over the references as applied to claim 1 above, and further in view of Ramachandran et al. (5,744,687).

The Examiner admits that Padin does not disclose the step of changing at least one of the pressure and temperature to release the alkene-rich component from the absorbent. However, he asserts that Ramachandran discloses a method of separating gaseous alkene (e.g., ethylene) from a gaseous alkane by an adsorption process. The desorption step of Ramachandran is operated at a temperature from about 100 to 350° C and at a pressure from about 20 to 5000 millibars. The Examiner concludes that it would have been obvious to one having ordinary skill in the art at the time the invention was made to have modified the process of Padin by changing pressure as taught by Ramachandran because such pressures and temperatures are effective to desorb alkene from the adsorbent.

Claims 27, 28, and 32 are rejected under 35 U.S.C. 103(b) as being unpatentable over Milton (2,882,243).

The Examiner points out that Milton discloses a process of adsorbing butadiene from a hydrocarbon feed mixture containing butene by using an A-zeolite adsorbent which comprises alkali and alkaline earth metal cations. He states that the adsorbing occurs at a temperature around 25 to 100° C and about 200 mmHg pressure and that the adsorbent is activated by heating it at a reduced pressure to remove adsorbed materials.

Regarding claim 28 and 32, the Examiner admits that Milton does not disclose the pressures and temperatures in the desorption step. However, he states that it would have been obvious to have modified the Milton process by desorbing butadiene from the adsorbent at a temperature from about 70 to 120° C at a pressure from 0.1 to 5 atm because Milton's adsorption temperature for butadiene is about 25° C and Milton also discloses that the conditions used for desorption of an adsorbate from zeolite A vary with the adsorbate and include raising the temperature and/or reducing the pressure. Therefore, the Examiner concludes that it would be effective to operate the desorption step by utilizing a temperature higher than 25° C (e.g., 70° C) and at a lower pressure (e.g., 1 atm) in the process of Milton.

The Examiner goes on to admit that, regarding claim 32, Milton does not disclose that sulfur compounds are contained in the feedstock. However, he concludes that it would have been obvious to modify the Milton process by utilizing a feedstock containing a tiny amount of hydrogen sulfide (e.g. 0.01 ppm) because it would be expected that the tiny amount of hydrogen sulfide present in the feedstock of Milton would not affect the outcome of the Milton process.

**ISSUE 1. Whether Padin, J. and R. T. Yang, "New Sorbents for Olefin/Paraffin Separations by Adsorption via  $\pi$ -Complexation: (I) Synthesis and Effects of Anions and Substrates," Chem. Eng. Sci., Vol. 55, p. 2607-2616 (2000) (Padin) is available as a § 103 reference against claims 1-10, 29 and 65 when the subject application was filed in the U.S. Patent Office less than one year after Padin's publication date?**

**Appellants answer: no**

**Examiner answers: yes**

In the Final Office Action dated August 26, 2003, the Examiner states that the Padin reference was "faxed on August 28, 1998" and takes the position that "the reference is known in 1998." Appellants take issue with the Examiner's position and respectfully request that the Padin reference be removed as a 103(a) reference. The first page of the fax referred to by the Examiner is attached as Exhibit 1. While the fax is dated August 28, 1998, that fax was sent by the inventors (note the fax indicia which indicate it was sent from "UM Chemical Eng") to the Appellants' attorney, Linda Deschere at Young & Basile, P.C., in order to assist in drafting a related application (which application was filed October 22, 1998 and matured into U.S. Patent No. 6,423,881). The fax was a confidential communication between the Appellants and the patent attorney, as opposed to a "publication" (as erroneously assumed by the Examiner). Also attached as Exhibit 2 is a portion of the letter from the University of Michigan dated August 20, 1998 (about a week before the fax date) to Ms. Deschere authorizing her to prepare and file a patent application on the subject matter of the fax. The letter instructs Ms. Deschere to work directly with the inventors regarding the technical aspects of the invention. Further, attached as Exhibit 3 is the first page of the actual published Padin paper, the official publication date of which is April 7, 2000.

The Appellants' above-identified application was filed August 7, 2000. Therefore, Appellants respectfully submit that the Padin reference is not available to the Examiner as a proper §103(a) reference. As such, Appellants request that the Padin reference be removed as a reference against the subject application.

**ISSUE 2. Whether the reference identified as "New Sorbents for Olefin/Paraffin Separations by Adsorption via  $\pi$ -Complexation," R.T. Yang and E.S. Kikkinides, *AIChE Journal*, Vol. 41, No. 3, pp. 509-517 (March 1995) complies with 37 C.F.R. 1.98(a)(2) which requires a legible copy of the reference cited, when it was legible enough for the Examiner to review and initial its citation on the Form PTO-1449 on April 16, 2001; and the Examiner cited it against pending claims in Office Actions dated April 24, 2001, October 18, 2001 and April 8, 2002?**

**Appellants answer: yes**

**Examiner answers: no**

The Examiner states that the AIChE 1995 Yang reference does not comply with 37 C.F.R. 1.98(a)(2) which requires a legible copy of the reference. As such, the Examiner states that the reference has been placed in the application file, yet the "information referred to therein has not been considered." This statement greatly puzzles Appellants. The Examiner has cited this very reference against pending claims in the above-identified application in at least three separate Office Actions. How could the "information referred to therein" not have been considered? Appellants submit that the AIChE 1995 Yang reference does comply with the provisions of 37 C.F.R. 1.98(a)(2), notification of which is respectfully requested.

**ISSUE 3. Whether claims 1-10, 27-29, 32 and 65 are patentable over Padin, J. and R. T. Yang, "New Sorbents for Olefin/Paraffin Separations by Adsorption via  $\pi$ -Complexation: (I) Synthesis and Effects of Anions and Substrates," *Chem. Eng. Sci.*, Vol. 55, p. 2607 (2000) (Padin) in view of Ogawa U.S. Patent No. 6,042,797, or further in view of Ramachandran et al., U.S. Patent No. 5,744,687 ('687) under 35 U.S.C. § 103(a); or alternately over Milton U.S. Patent No. 2,882,243 under 35 U.S.C. § 103(b), when none of the references teach or suggest a method effective for use in the presence of hydrogen sulfide, the hydrogen sulfide present in amounts normally present in conventional cracked gas streams?**

**Appellants answer: yes**

**Examiner answers: no**

Assuming *arguendo* that the Padin reference were available, it is submitted that the Padin/Yang manuscript nowhere teaches, suggests or discloses a method for separating hydrocarbons in the presence of hydrogen sulfide present in amounts normally present in conventional cracked gas streams. Absent any such teaching, the skilled artisan is well aware that hydrogen sulfide poisons sorbents, catalysts, etc., thus generally rendering them ineffective. It was highly unexpected and counter-intuitive to discover that the sorbents as recited in the pending claims substantially maintain their adsorbent capacity and preference for the alkene or diene in the presence of the hydrogen sulfide.

The skilled artisan recognizes that the presence of sulfur compounds is generally known to have deleterious effects in various petroleum refining processes. See, for example, the specification as filed at page 3, lines 3 et seq. In this area of the specification, the Appellants teach that the presence of sulfur in amounts greater than about 2 or 3 ppm is generally harmful to material(s) used in refining processes. In contrast, a conventional cracked gas stream before any desulfurizing distillation steps contains hydrogen sulfide present in amounts of about 0.01 mole% (100 ppm). (See specification at page 13, lines 12-22).

Appellants respectfully submit to the Examiner that Appellants' invention as defined in claims 1, 15, 29, 32, 34 and 48 is predicated on the fact that it is not necessary to desulfurize to extremely low levels:

[T]his novel adsorbent fortuitously and unexpectedly substantially maintains its adsorbent capacity and preference for the alkene in the presence of the sulfur compound. This is highly desirable, as this sulfur tolerant and/or resistant adsorbent (as well as the other novel adsorbents described hereinbelow) **obviates step(s) conventionally necessary to desulfurize the cracked gas stream(s).** (emphasis added) page 10, lines 28-36.

The Examiner is further directed to the instant application at page 13, lines 13-22:

The novel adsorbents were exposed to very severe amounts, for example the hydrogen sulfide was present in amounts up to about 66 mole%. **In sharp contrast, a conventional cracked gas stream before any desulfurizing distillation steps contains hydrogen sulfide present in amounts of about 0.01 mole% [100 ppm].** As such, the data presented hereinbelow indicate that **the novel adsorbents of the present invention**

**would be quite robust, ie. very tolerant and/or resistant to H<sub>2</sub>S under normal operating conditions.** (emphasis added)

The Examiner asserts that the Appellants' invention as defined in claims 1 and 29 would be obvious because one would have known to modify the process of Padin by "using an olefinic feed comprising hydrogen sulfide because sulfur compounds would not affect the outcome of the process." Given the statements above regarding the deleterious effects of sulfur in refining processes, it is submitted that the Examiner has engaged in impermissible hindsight in order to make this assertion.

Further, Appellants point out that Ogawa states at Col. 6, lines 29 that "[t]he adsorbent is effective also in a case where the gas contains not only ethylene but also . . . sulfur oxide." In Ogawa, the olefins are being removed from the atmosphere or an exhaust gas. Exhaust gas contains by-products of burning: sulfur oxides, carbon oxides, etc. In Appellants' invention as defined in claims 1, 15, 29, 32, 34 and 48, it is recited that the adsorbent substantially maintains its adsorbent capacity and selectivity in the presence of hydrogen sulfide. This is remarkable in that hydrogen sulfide has been recognized as being capable of potentially deactivating entire adsorbents. **Thus, hydrogen sulfide has been recognized as reacting detrimentally; whereas sulfur oxide may in some instances be a substantially inert by-product.**

Alternately, Ogawa et al. themselves teach that sulfur oxide may not necessarily be that inert. Ogawa '797 teaches silver exchanged ferrierite (or ZSM-5) zeolite only, for adsorption of ethylene. In Example 26 of Ogawa, the inventors used Ag-ZSM-5 as a catalyst for NO reduction in flue gas. In this example, they included 25 ppm SO<sub>2</sub> in the gas feed. They showed very low catalytic activities (the NO conversion was very low at a very low space velocity, or very long contact time). The inventors did not remark on the effect of SO<sub>2</sub> addition. Yet, from their own data, SO<sub>2</sub> clearly poisoned the catalyst. It is submitted that this **teaches away** from the Examiner's assertion that Ogawa teaches that sulfur compounds would not affect the outcome of the process.

It is respectfully submitted that the Examiner has used impermissible hindsight from Applicants' disclosure in order to **assume** that Ogawa teaches or even suggests a gas stream having hydrogen sulfide therein. It is further submitted that, in doing so, the Examiner has made errors in logic and consequently in the technical field at hand.

The Federal Circuit has spoken to the issue of impermissible hindsight on numerous occasions. In *In re David H. Fine*, 837 F.2d 1071, 5 U.S.P.Q. (BNA) 1596 (Fed. Cir. 1988), the court stated:

To reach a proper conclusion under § 103, the decisionmaker must step backward in time and into the shoes worn by [a person having ordinary skill in the art] when the invention was unknown and just before it was made. In light of *all* the evidence, the decisionmaker must then determine whether . . . the claimed invention as a whole would have been obvious at *that* time to *that* person. 35 U.S.C. § 103. The answer to that question partakes more of the nature of law than of fact, for it is an ultimate conclusion based on a foundation formed of all the probative facts. (emphasis in original) *Id.* at 1073-74, quoting *Panduit Corp. v. Dennison Mfg. Co.*, 810 F.2d 1561, 1566 (Fed. Cir. 1987)

Further, the *Fine* court stated at 1075:

Because neither Warnick nor Eads, alone or in combination, suggests the claimed invention, the Board erred in affirming the Examiner's conclusion that it would have been obvious to substitute the Warnick nitric oxide detector for the Eads sulfur dioxide detector in the Eads system. *ACS Hosp. Sys.*, 732 F.2d at 1575-77, 221 USPQ at 931-33. **The Eads and Warnick references disclose, at most, that one skilled in the art might find it obvious to try the claimed invention. But whether a particular combination might be "obvious to try" is not a legitimate test of patentability.** [references omitted] (emphasis added)

The first quote above from the *Fine* court makes it clear that the Examiner must "step backward in time" to just before the present invention was made, and look at Padin and Ogawa **without knowledge gleaned from Appellants' disclosure**. If the Examiner did this, in light of the detailed discussion above of what the skilled artisan would glean from the reference, he would come to the conclusion that neither reference speaks to the issue of hydrogen sulfide at all.

The Examiner's assertion seems to be that the skilled artisan would find it "obvious to try" to run a gas stream having hydrogen sulfide therein over the sorbents of the references. **"But whether a particular combination might be 'obvious to try' is not a legitimate test of patentability."** *Id.* (emphasis added)

Obviousness is tested by what the combined teaching of the references would have suggested to those of ordinary skill in the art. See *In re Keller*, 642 F.2d 413, 425, 208 U.S.P.Q. (BNA) 871, 881 (CCPA 1981). Approaches to obviousness determinations which focus merely on identifying and tabulating missing elements in hindsight retrospect imbue one of ordinary skill in the art with knowledge of the invention in suit, when no prior art reference or references of record convey or suggest

that knowledge (ie. that Padin's sorbent adequately functions in the presence of hydrogen sulfide), and fall victim to the insidious effect of the hindsight syndrome wherein that which only the inventor taught is used against its teacher. (emphasis added). *W.L. Gore & Assoc. v. Garlock, Inc.*, 721 F.2d 1540, 1553, 220 U.S.P.Q. (BNA) 312, 313 (Fed. Cir. 1983).

The Examiner asserts that because Padin does not disclose that the adsorbent is *incapable* of adsorbing olefins in the presence of hydrogen sulfide and that the adsorbent is the same as the Appellants, the Padin adsorbent would be *expected* to be capable of adsorbing olefins in the presence of hydrogen sulfide. However, this assertion and conclusion, without engaging in impermissible hindsight, flies in the face of what the skilled artisan knew to be true at the time the invention was made, that hydrogen sulfide generally poisoned sorbents. Further, the skilled artisan looks to references for what they fairly teach, not for everything they do not teach. As such, the Examiner's assertion that Padin does disclose that the adsorbent is incapable in the presence of hydrogen sulfide erroneously changes the standard of treatment of references by the skilled artisan.

Neither Padin nor Ogawa disclose a method utilizing adsorbents that substantially maintain their adsorbent capacity and selectivity in the presence of hydrogen sulfide as recited in Appellants' claims 1, 15, 29, 32, 34 and 48. As such, it is submitted that Appellants' invention as defined in these claims, as well as in all claims dependent therefrom, is not anticipated, taught or rendered obvious by Padin or Ogawa, either alone or in combination, and patentably defines over the art of record.

Regarding claims 65-68, the Examiner admits that Padin does not disclose that the alkene feedstock is a conventional cracked gas stream before any desulfurizing distillation steps, however, he asserts that it would have been obvious to modify the process of Padin by using the claimed feedstock.

Appellants disagree with the Examiner's assertion and respectfully submit that the assertion is illogical. Neither Padin nor Ogawa teach, suggest, or disclose anything about hydrogen sulfide. Further, as shown in the specification itself and as is generally known in the art, hydrogen sulfide in amounts greater than about 2 or 3 ppm deleteriously affects sorbents, catalysts, etc. in refining processes. As such, the skilled artisan would NOT expect that the results would be similar when using a feedstock

containing hydrogen sulfide present in amounts normally present in conventional cracked gas streams. As such, it is submitted that Appellants' invention as defined in claim 65-68 is not anticipated, taught or rendered obvious by Padin or Ogawa, either alone or in combination, and patentably defines over the art of record.

Claims 8 and 9 stand rejected under Padin in view of Ogawa and further in view of Ramachandran. The Examiner asserts that it would have been obvious to have modified the process of Padin by changing the temperature and pressure as taught by Ramachandran because such temperatures and pressures are effective to desorb alkenes from the adsorbent.

Appellants reassert the notion that the Examiner is assuming that modifying the process of Padin will produce the same results, even in the presence of hydrogen sulfide. However, the skilled artisan is well aware (as discussed above), that hydrogen sulfide poisons sorbents, catalysts, etc., thus generally rendering them ineffective. Changing the temperature and pressure would not eliminate the presence of the hydrogen sulfide. Therefore, one skilled in the art would not have expected that by modifying the temperature and pressure of the Padin process that they would have been able to effectively adsorb in the presence of hydrogen sulfide.

Claims 27, 28 and 32 stand rejected under 35 U.S.C. § 103(b) as being unpatentable over Milton. As previously stated, the Examiner admits that Milton does not disclose the pressures and temperatures in the desorption step. He further states that it would have been obvious to have modified the Milton process by desorbing butadiene from the adsorbent at a temperature between 70°C and 120°C and at a pressure between 0.1 and 5 atm because Milton's adsorption temperature for butadiene is about 25°C and Milton also discloses that the conditions used for desorption of an adsorbate from zeolite A vary with the adsorbate and include raising the temperature and/or reducing the pressure. The Examiner also concludes that it would have been obvious to modify the Milton process by utilizing a feedstock containing a tiny amount of hydrogen sulfide (e.g. 0.01 ppm) because it would be expected that the tiny amount of hydrogen sulfide present in the feedstock of Milton would not affect the outcome of the Milton process in a short run.



The Examiner appears to be ignoring the claim recitation that the hydrogen sulfide is present in amounts up to about 66 mole%. None of the cited references teach or suggest adsorbents that can function in an atmosphere having up to about 66 mole% hydrogen sulfide present (as stated above, in fact they do not even mention hydrogen sulfide).

As previously stated, hydrogen sulfide poisons sorbents, catalysts, etc., thus generally rendering them ineffective. It would NOT have been obvious to subject the feedstock of Milton to even small amounts of hydrogen sulfide for a short run because of the likelihood of rendering them ineffective.

Applicants further do not acquiesce to the Examiner's conclusion, as it begs the issue, and is also not practical. As stated in Applicants' application at page 3, lines 5-10:

[I]n catalytic reforming, the catalyst used is often platinum supported on high-purity alumina. However, the platinum on the catalyst is seriously deactivated by sulfur compounds, and therefore the feedstock is desulfurized to less than **3 ppm** by weight of sulfur before the reforming.

In order to preserve the expensive platinum in a catalytic reforming process, the desulfurization is taken substantially to the limits--in other processes, one would generally not see feedstocks having as low as 3 ppm hydrogen sulfide. **As such, it would be extremely expensive and time consuming, if not impossible, to desulfurize feedstock to a level of "0.01 ppm" as suggested by the Examiner.**

At best, modifying the Milton process in the presence of hydrogen sulfide might be obvious to try, however, whether a particular combination might be "obvious to try" is not a legitimate test of patentability. *In re Fine*, 837 F.2d at 1075. As such, it is submitted that Appellants' invention as defined in claims 27, 28 and 32, as well as in any claims dependent therefrom, is not anticipated, taught, or rendered obvious by Milton, either alone or in combination, and patentably defines over the art of record.

For all the above reasons, it is submitted that Appellants' invention as defined in claims 1-10, 15-25, 27-29, 31, 32, 34-54 and 65-68 is not anticipated, taught or rendered obvious by Padin, Ogawa, Ramachandran, or Milton, either alone or in combination, and patentably defines over the art of record.

It is further submitted that the arguments for patentability of the claims hereinabove and hereinbelow are intended to be cumulative.

**ISSUE 4. Whether claim 10 is patentable over Padin, J. and R. T. Yang, "New Sorbents for Olefin/Paraffin Separations by Adsorption via  $\pi$ -Complexation: (I) Synthesis and Effects of Anions and Substrates," Chem. Eng. Sci., Vol. 55, p. 2607 (2000) (Padin) in view of Ogawa U.S. Patent No. 6,042,797, when Ogawa teaches away from a method utilizing  $\pi$ -complexation, and there is no suggestion or motivation to combine Ogawa with Padin?**

Appellants answer: yes

Examiner answers: no

Ogawa does not ever mention  $\pi$ -complexation, and in fact teaches away from bonding by  $\pi$ -complexation. Ogawa states that the sorbent has a "strong power for holding the adsorbed hydrocarbon," Col 3, line 45-46, and that it desorbs "starting at" 200C to 300C. As stated in the specification,  $\pi$ -complex bonds are relatively weak. Further, Appellants recite that desorption takes place starting at about 70C.  $\pi$ -complexation occurs with d-block transition metals, however, Ogawa states that any transition metals may be used (Col. 6, lines 6 et seq). This points away from Ogawa even contemplating  $\pi$ -complexation bonding.

As such, the Examiner has offered no motivation to combine Padin with Ogawa. The Federal Circuit spoke to this issue in the recent case of *In re Lee*, 277 F.3d 1338, 61 U.S.P.Q.2d (BNA) 1430 (Fed. Cir. 2002):

With respect to Lee's application, neither the examiner nor the Board adequately supported the selection and combination of the Nortrup and Thunderchopper references to render obvious that which Lee described. The examiner's **conclusory statements** that "the demonstration mode is just a programmable feature which can be used in many different devices for providing automatic introduction by adding the proper programming software" and that "another motivation would be that the automatic demonstration mode is user friendly and it functions as a tutorial" do not adequately address the issue of motivation to combine. **This factual question [\*1344] of motivation is material to patentability, and could not be resolved on subjective belief and unknown authority.** It is improper, in determining whether a person of ordinary skill would have been led to this combination of references, simply to "[use] that which the inventor taught against its teacher." *W.L. Gore v. Garlock, Inc.*, 721 F.2d 1540, 1553, 220 U.S.P.Q. (BNA) 303, 312-13 (Fed. Cir. 1983). Thus the

Board must not only assure that the requisite findings are made, based on evidence of record, but must also explain the reasoning by which the findings are deemed to support the agency's conclusion. (emphasis added)

It is submitted that the Examiner has not provided any evidence regarding motivation to support combination of the two references. For this further reason, it is submitted that claim 10 is not anticipated, taught or rendered obvious by any of the cited references, and patentably defines over the art of record.

**ISSUE 5. Whether claims 65-68 are patentable over Padin, J. and R. T. Yang, "New Sorbents for Olefin/Paraffin Separations by Adsorption via  $\pi$ -Complexation: (I) Synthesis and Effects of Anions and Substrates," Chem. Eng. Sci., Vol. 55, pp. 2607-2616 (2000) (Padin) in view of Ogawa U.S. Patent No. 6,042,797, when none of the references teach or suggest a method wherein the gaseous mixture is contained in a conventional cracked gas stream before any desulfurizing distillation steps occur?**

Appellants answer: yes

Examiner answers: no

The Examiner admits that Padin does not disclose that the alkene feedstock is a conventional cracked gas stream before any desulfurizing distillation steps, however, he asserts that it would have been obvious to modify the process of Padin by using the claimed feedstock.

Appellants disagree with the Examiner's assertion and respectfully submit that the assertion is illogical. Neither Padin nor Ogawa teach, suggest, or disclose anything about hydrogen sulfide. Further, as shown in the specification itself and as is generally known in the art, hydrogen sulfide in amounts greater than about 2 or 3 ppm deleteriously affects sorbents, catalysts, etc. in refining processes. A conventional cracked gas stream **before** any desulfurizing distillation steps contains hydrogen sulfide present in amounts of about 0.01 mole% (100 ppm). (See specification at page 13, lines 12-22).

The skilled artisan would NOT expect that the results would be similar when using a feedstock containing hydrogen sulfide present in amounts normally present in conventional cracked gas streams. As such, it is submitted that Appellants' invention

as defined in claim 65-68 is not anticipated, taught or rendered obvious by any of the cited references, and patentably defines over the art of record.

**ISSUE 6. Whether claims 15-25, 27, 28, 31, 32, 34-54 and 66-68 are patentably distinct from claims 1-26 of U.S. Patent No. 6,215,037, when the reference does not teach or suggest a method for separating a diene from a mixture including the diene and hydrogen sulfide, the hydrogen sulfide present in amounts normally present in conventional cracked gas streams?**

Appellants answer: yes

Examiner answers: no

The '037 patent neither teaches nor suggests a method of separating hydrocarbons as claimed in a gaseous mixture which includes hydrogen sulfide present in amounts normally present in conventional cracked gas streams, as recited in Applicants' invention as defined in claims 15, 32, 34 and 48.

As previously stated, the skilled artisan recognizes that the presence of sulfur compounds is generally known to have deleterious effects in various petroleum refining processes. See, for example, the specification as filed at page 3, lines 3 et seq. In this area of the specification, the Appellants teach that the presence of sulfur at amounts greater than about 2 or 3 ppm is generally harmful to material(s) used in refining processes. In contrast, a conventional cracked gas stream before any desulfurizing distillation steps contains hydrogen sulfide present in amounts of about 0.01 mole% (100 ppm). (See specification at page 13, lines 12-22).

Appellants' invention as defined in claim 32 recites that the hydrogen sulfide is present in amounts up to about 66 mole%.

Since the '037 patent neither teaches nor suggests hydrocarbon separations in a gaseous mixture containing hydrogen sulfide present in amounts normally present in conventional cracked gas streams, much less in amounts up to about 66 mole%, it is submitted that Appellants' invention as defined in independent claims 15, 32, 34 and 48, as well as in any claims ultimately dependent therefrom, has obviated the rejection under the judicially created doctrine of obviousness-type double patenting.

In the event that the remaining rejections (other than obviousness-type double patenting) are removed, Appellants submit that they will consider filing a terminal disclaimer in compliance with 37 C.F.R. 1.321(c) in order to expedite prosecution of the above-identified application.

**ISSUE 7. Whether claims 1-10, 29 and 65 are patentably distinct from claims 1-19 of U.S. Patent No. 6,426,881 when the reference does not teach or suggest a method of separating gaseous alkene selected from the group consisting of ethylene, propylene and mixtures thereof, from a gaseous mixture including the alkene and hydrogen sulfide, the hydrogen sulfide present in amounts normally present in conventional cracked gas streams?**

Appellants answer: yes

Examiner answers: no

The '881 patent neither teaches nor suggests a method of separating hydrocarbons as claimed in a gaseous mixture which includes hydrogen sulfide present in amounts normally present in conventional cracked gas streams, as recited in Applicants' invention as defined in claims 1 and 29.

As previously stated, the skilled artisan recognizes that the presence of sulfur compounds is generally known to have deleterious effects in various petroleum refining processes. See, for example, the specification as filed at page 3, lines 3 et seq. In this area of the specification, the Appellants teach that the presence of sulfur at amounts greater than about 2 or 3 ppm is generally harmful to material(s) used in refining processes. In contrast, a conventional cracked gas stream before any desulfurizing distillation steps contains hydrogen sulfide present in amounts of about 0.01 mole% (100 ppm). (See specification at page 13, lines 12-22).

Appellants' invention as defined in claim 29 recites that the hydrogen sulfide is present in amounts up to about 66 mole%.

Since the '881 patent neither teaches nor suggests hydrocarbon separations in a gaseous mixture containing hydrogen sulfide present in amounts normally present in conventional cracked gas streams, much less in amounts up to about 66 mole%, it is submitted that Appellants' invention as defined in independent claims 1 and 29, as well

as in any claims ultimately dependent therefrom, has obviated the rejection under the judicially created doctrine of obviousness-type double patenting.

In the event that the remaining rejections (other than obviousness-type double patenting) are removed, Appellants submit that they will consider filing a terminal disclaimer in compliance with 37 C.F.R. 1.321(c) in order to expedite prosecution of the above-identified application.

In summary,

1) The Padin reference was published in 2000, therefore, is not a proper reference under 35 U.S.C. § 103(a). Appellants submit that the fax of the reference in 1998 was to Appellants' attorney and thus was a confidential communication rather than a publication.

2) Neither the Padin nor the Ogawa reference teach or suggest Appellants' the method as defined in the pending claims in the presence of hydrogen sulfide in amounts normally present in conventional cracked gas streams. In fact, one skilled in the art would not expect to subject the Padin adsorbent to hydrogen sulfide because hydrogen sulfide was known generally to poison sorbents, catalysts, etc., thus generally rendering them ineffective. In sharp contrast, the Appellants' adsorbents were exposed even to very severe amounts of hydrogen sulfide, for example amounts up to about 66 mole%, while effectively maintaining capacity and selectivity.

3) Appellants teach that the presence of sulfur at amounts greater than about 2 or 3 ppm is generally harmful to material(s) used in refining processes. In contrast, a conventional cracked gas stream before any desulfurizing distillation steps contains hydrogen sulfide present in amounts of about 0.01 mole% (100 ppm). Appellants' method as defined in the pending claims introduces the sorbents into a conventional cracked gas stream **before** any desulfurizing distillation steps.

4) Milton teaches a process for adsorbing butadiene from a hydrocarbon feed mixture by using an A-zeolite in the absence of hydrogen sulfide. Appellants' invention as defined in claims 1, 15, 29, 32, 34 and 48 recites that the adsorbents are subjected to hydrogen sulfide present in amounts normally present in conventional cracked gas streams.

CONCLUSION

For the reasons stated above, it is submitted that the Padin reference is not available as a proper 35 U.S.C. § 103(a) reference. Assuming *arguendo* the reference is available, there is no teaching or suggestion in either of Padin, Ogawa, Ramachandran or Milton, of a method utilizing an adsorbent able to substantially maintain its capacity and selectivity in the presence of hydrogen sulfide. It is further submitted that the Examiner has not made his prima facie case of obviousness with regard to the claims reciting  $\pi$ -complexation for bonding, nor for the claims reciting that the gaseous mixture is contained in a conventional cracked gas stream before any desulfurizing distillation steps.

Thus, it is respectfully submitted that Appellants' invention as set forth in claims 1-10, 15-25, 27-29, 31, 32, 34-54 and 65-68 patentably defines over the cited references and is not anticipated, taught or rendered obvious thereby. As such, it is respectfully submitted that the Examiner's final rejection of claims 1-10, 15-25, 27-29, 31, 32, 34-54 and 65-68 is erroneously based, and its reversal is respectfully requested.

No oral hearing is requested.

This Appeal Brief is being filed in triplicate, including one original and two copies.

Respectfully submitted,

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APPENDIX

CLAIMS AT ISSUE IN APPEAL OF S.N. 09/632,891

1. A method of separating gaseous alkene selected from the group consisting of ethylene, propylene and mixtures thereof, from a gaseous mixture including the alkene and hydrogen sulfide, the hydrogen sulfide present in amounts normally present in conventional cracked gas streams, the method comprising the steps of:

contacting the gaseous mixture with an adsorbent which preferentially adsorbs the alkene, at a selected temperature and pressure, thereby producing a non-adsorbed component and an alkene-rich adsorbed component; the adsorbent comprising a carrier having a surface area, the carrier having a monolayer of a silver compound dispersed on substantially the entire surface area, the silver compound releasably retaining the alkene; and the carrier comprising a plurality of pores having a pore size greater than the effective molecular diameter of the alkene; and

changing at least one of the pressure and temperature to thereby release the alkene-rich component from the adsorbent;

wherein the adsorbent substantially maintains its adsorbent capacity and preference for the alkene in the presence of the hydrogen sulfide.

2. The method as defined in claim 1 wherein the silver compound is silver nitrate ( $\text{AgNO}_3$ ) and the carrier is silica ( $\text{SiO}_2$ ).

3. The method as defined in claim 1 wherein the silver compound is a silver salt, and wherein the salt is selected from the group consisting of acetate, benzoate, bromate, chlorate, perchlorate, chlorite, citrate, fluoride, nitrate, nitrite, sulfate, and mixtures thereof.

4. The method as defined in claim 1 wherein the carrier has a BET surface area greater than about 50 square meters per gram and up to about 2,000 square meters per gram, and comprises a plurality of pores having a pore size greater than about 3 angstroms and up to about 10 microns.



5. The method as defined in claim 1 wherein the carrier is a high surface area support selected from the group consisting of refractory inorganic oxide, molecular sieve, activated carbon, and mixtures thereof.

6. The method as defined in claim 5 wherein the refractory inorganic oxide is selected from the group consisting of pillared clay, alumina and silica.

7. The method as defined in claim 1 wherein the silver compound is a silver (I) halide and the carrier is silica.

8. The method as defined in claim 1 wherein the selected pressure of preferential adsorption is a first pressure, and the pressure of release is a second pressure less than the first pressure, and wherein the first pressure is in a range of about 1 atmosphere to about 35 atmospheres, and further wherein the second pressure is in a range of about 0.01 atm to about 5 atm.

9. The method as defined in claim 1 wherein the selected temperature of preferential adsorption is a first temperature, and the temperature of release is a second temperature greater than the first temperature, and wherein the first temperature is in a range of about 0°C to about 50°C, and further wherein the second temperature is in a range of about 70°C to about 200°C.

10. The method as defined in claim 1 wherein the retaining of the alkene is accomplished by formation of  $\pi$ -complexation bonds between the silver compound and the alkene.

15. A method for separating a diene from a mixture including the diene and hydrogen sulfide, the hydrogen sulfide present in amounts normally present in conventional cracked gas streams, the method comprising the step of:

contacting the mixture with an adsorbent which preferentially adsorbs the diene, at a selected temperature and pressure, thereby producing a non-adsorbed component and a diene-rich adsorbed component, wherein the adsorbent comprises an ion-exchanged zeolite selected from the group consisting of zeolite X, zeolite Y, zeolite LSX, and mixtures thereof, the zeolite having exchangeable cationic sites, and a majority of the sites having silver cation or copper cation present, and wherein the preferential adsorption occurs by  $\pi$ -complexation, and further wherein the adsorbent substantially maintains its adsorbent capacity and preference for the diene in the presence of the hydrogen sulfide.

16. The method as defined in claim 15 wherein the diene is selected from the group consisting of butadiene, hexadiene, octadiene and mixtures thereof, and wherein the method further comprises the step of changing at least one of the pressure and temperature to thereby release the diene-rich component from the adsorbent.

17. The method as defined in claim 15 wherein the diene is 1,3-butadiene, and wherein the mixture includes 1,3-butadiene and at least one other C<sub>4</sub> unsaturated compound.

18. The method as defined in claim 15 wherein the majority of the cationic sites of the ion-exchanged zeolite contain the silver cation.

19. The method as defined in claim 15 wherein the majority of the cationic sites of the ion-exchanged zeolite contain the copper cation.

20. The method as defined in claim 15 wherein the mixture comprises at least one mono-olefin having as many carbon atoms as the diene, wherein the diene is selected from the group consisting of butadiene, hexadiene, octadiene, and mixtures thereof; and wherein the mono-olefin is selected from the group consisting of butene, hexene, octene, and mixtures thereof.

21. The method as defined in claim 20 wherein the mono-olefin is butene and the diene is butadiene.

22. The method as defined in claim 20 wherein the mixture comprises the mono-olefin in a gaseous state and saturated with the diene.

23. The method as defined in claim 15 wherein essentially all cationic sites of the ion-exchanged zeolite contain the silver cation.

24. The method as defined in claim 16 wherein the selected pressure of preferential adsorption is a first pressure, and the pressure of release is a second pressure less than the first pressure, wherein the first pressure is in a range of about 1 atmosphere to about 35 atmospheres, and wherein the second pressure is in a range of about 0.01 atmosphere to about 5 atmospheres.

25. The method as defined in claim 16 wherein the selected temperature of preferential adsorption is a first temperature, and the temperature of release is a second temperature greater than the first temperature, wherein the first temperature is in a range of about 0°C to about 150°C, and wherein the second temperature is in a range of about 70°C to about 250°C.

27. The method as defined in claim 32 wherein the diene is selected from the group consisting of butadiene, hexadiene, octadiene, and mixtures thereof.

28. The method as defined in claim 27 wherein a selected pressure of preferential adsorption is a first pressure, and a pressure of release is a second pressure less than the first pressure, wherein the first pressure is in a range of about 1 atmosphere to about 35 atmospheres, and wherein the second pressure is in a range of about 0.01 atmosphere to about 5 atmospheres.

29. A method of separating gaseous alkene selected from the group consisting of ethylene, propylene and mixtures thereof, from a gaseous mixture including the alkene and a sulfur compound, the method comprising the steps of:

contacting the gaseous mixture with an adsorbent which preferentially adsorbs the alkene, at a selected temperature and pressure, thereby producing a non-adsorbed component and an alkene-rich adsorbed component; the adsorbent comprising a carrier having a surface area, the carrier having a monolayer of a silver compound dispersed on substantially the entire surface area, the silver compound releasably retaining the alkene; and the carrier comprising a plurality of pores having a pore size greater than the effective molecular diameter of the alkene; and

changing at least one of the pressure and temperature to thereby release the alkene-rich component from the adsorbent;

wherein the adsorbent substantially maintains its adsorbent capacity and preference for the alkene in the presence of the sulfur compound, wherein the sulfur compound is hydrogen sulfide, and wherein the hydrogen sulfide is present in amounts up to about 66 mole%.

31. The method as defined in claim 15 wherein the hydrogen sulfide is present in amounts up to about 66 mole%.

32. A method for separating a diene from a mixture including the diene and a sulfur compound, the method comprising the steps of:

contacting the mixture with an adsorbent which preferentially adsorbs the diene at a first temperature, thereby producing a non-adsorbed component and a diene-rich adsorbed component, wherein the adsorbent comprises zeolite A having exchangeable cationic sites, a plurality of the zeolite A sites having an alkali metal cation or an alkaline earth metal cation present; and

releasing the diene-rich adsorbed component from the adsorbent by elevating the temperature to a second temperature which ranges between about 70°C and about 120°C;

wherein the adsorbent substantially maintains its adsorbent capacity and preference for the diene in the presence of the sulfur compound, wherein the sulfur compound is hydrogen sulfide, and wherein the hydrogen sulfide is present in amounts up to about 66 mole%.

34. A method for separating a diene from a mixture including the diene and hydrogen sulfide, the hydrogen sulfide present in amounts normally present in conventional cracked gas streams, the method comprising the step of:

contacting the mixture with an adsorbent which preferentially adsorbs the diene, at a selected temperature and pressure, thereby producing a non-adsorbed component and a diene-rich adsorbed component, wherein the adsorbent comprises an ion-exchanged zeolite selected from the group consisting of zeolite X, zeolite Y, zeolite LSX, and mixtures thereof, the zeolite having exchangeable cationic sites, and at least some of the sites having silver cation or copper cation present, and wherein the preferential adsorption occurs by  $\pi$ -complexation, and further wherein the adsorbent substantially maintains its adsorbent capacity and preference for the diene in the presence of the hydrogen sulfide.

35. The method as defined in claim 34 wherein the diene is selected from the group consisting of butadiene, hexadiene, octadiene and mixtures thereof, and wherein the method further comprises the step of changing at least one of the pressure and temperature to thereby release the diene-rich component from the adsorbent.

36. The method as defined in claim 34 wherein the diene is 1,3-butadiene, and wherein the mixture includes 1,3-butadiene and at least one other C<sub>4</sub> unsaturated compound.

37. The method as defined in claim 34 wherein a majority of the cationic sites of the ion-exchanged zeolite contain the silver cation.

38. The method as defined in claim 34 wherein a majority of the cationic sites of the ion-exchanged zeolite contain the copper cation.

39. The method as defined in claim 34 wherein the mixture comprises at least one mono-olefin having as many carbon atoms as the diene, wherein the diene is selected from the group consisting of butadiene, hexadiene, octadiene, and mixtures thereof; and wherein the mono-olefin is selected from the group consisting of butene, hexene, octene, and mixtures thereof.

40. The method as defined in claim 39 wherein the mono-olefin is butene and the diene is butadiene.

41. The method as defined in claim 39 wherein the mixture comprises the mono-olefin in a gaseous state and saturated with the diene.

42. The method as defined in claim 34 wherein essentially all cationic sites of the ion-exchanged zeolite contain the silver cation.

43. The method as defined in claim 35 wherein the selected pressure of preferential adsorption is a first pressure, and the pressure of release is a second pressure less than the first pressure, wherein the first pressure is in a range of about 1 atmosphere to about 35 atmospheres, and wherein the second pressure is in a range of about 0.01 atmosphere to about 5 atmospheres.

44. The method as defined in claim 35 wherein the selected temperature of preferential adsorption is a first temperature, and the temperature of release is a second temperature greater than the first temperature, wherein the first temperature is in a range of about 0°C to about 150°C, and wherein the second temperature is in a range of about 70°C to about 250°C.

45. The method as defined in claim 34 wherein the at least some of the sites have silver cation present.

46. The method as defined in claim 34 wherein the at least some of the sites have copper cation present.

47. The method as defined in claim 34 wherein essentially all cationic sites of the ion-exchanged zeolite contain the copper cation.

48. A method for separating a diene from a mixture including the diene and hydrogen sulfide, the hydrogen sulfide present in amounts normally present in conventional cracked gas streams, wherein the diene is selected from the group consisting of butadiene, hexadiene, octadiene and mixtures thereof, wherein the mixture comprises at least one mono-olefin having as many carbon atoms as the diene, and wherein the mono-olefin is selected from the group consisting of butene, hexene, octene, and mixtures thereof, the method comprising the steps of:

contacting the mixture with an adsorbent which preferentially adsorbs the diene, at a selected temperature and pressure, thereby producing a non-adsorbed component and a diene-rich adsorbed component, wherein the adsorbent comprises an ion-exchanged zeolite selected from the group consisting of zeolite X, zeolite Y, zeolite LSX, and mixtures thereof, the zeolite having exchangeable cationic sites, and at least some of the sites having silver cation or copper cation present, and wherein the preferential adsorption occurs by  $\pi$ -complexation, and further wherein the adsorbent substantially maintains its adsorbent capacity and preference for the diene in the presence of the hydrogen sulfide;

changing at least one of the pressure and temperature to thereby release the diene-rich component from the adsorbent, wherein the selected pressure of preferential adsorption is a first pressure, and the pressure of release is a second pressure less than the first pressure, wherein the first pressure is in a range of about 1 atmosphere to about 35 atmospheres, and wherein the second pressure is in a range of about 0.01 atmosphere to about 5 atmospheres;

and wherein the selected temperature of preferential adsorption is a first temperature, and the temperature of release is a second temperature greater than the first temperature, wherein the first temperature is in a range of about 0°C to about 150°C, and wherein the second temperature is in a range of about 70°C to about 250°C.

49. The method as defined in claim 48 wherein the mono-olefin is butene and the diene is butadiene.

50. The method as defined in claim 48 wherein the mixture comprises the mono-olefin in a gaseous state and saturated with the diene.

51. The method as defined in claim 48 wherein a majority of the sites have silver cation present.

52. The method as defined in claim 48 wherein a majority of the sites have copper cation present.

53. The method as defined in claim 48 wherein essentially all cationic sites of the ion-exchanged zeolite contain the copper cation.

54. The method as defined in claim 48 wherein essentially all cationic sites of the ion-exchanged zeolite contain the silver cation.

65. The method as defined in claim 1 wherein the gaseous mixture is contained in a conventional cracked gas stream before any desulfurizing distillation steps.

66. The method as defined in claim 15 wherein the gaseous mixture is contained in a conventional cracked gas stream before any desulfurizing distillation steps.

67. The method as defined in claim 34 wherein the gaseous mixture is contained in a conventional cracked gas stream before any desulfurizing distillation steps.



68. The method as defined in claim 48 wherein the gaseous mixture is contained in a conventional cracked gas stream before any desulfurizing distillation steps.

**Exhibit 1**

S.N. 09/632,891

**New Sorbents for Olefin/Paraffin Separations by Adsorption via  $\pi$ -Complexation: (I) Synthesis and Effects of Anions and Substrates**

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**ABSTRACT**

New adsorbents for olefin/paraffin separations are synthesized by effective dispersion of  $\text{Ag}^+$  cations on high-surface-area substrates. Two techniques for synthesis are compared: thermal monolayer dispersion and incipient wetness impregnation. Monolayer  $\text{AgNO}_3$  is dispersed on three substrates ( $\gamma\text{-Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and MCM-41 mesoporous molecular sieve) for ethane/ethylene and propane/propylene separations. The incipient wetness technique yields the best sorbents that show the highest selectivities, olefin capacities, reversibility and fast rates. The surface chemistry of the substrate plays an important role in olefin adsorption. The silica surface (on both silica gel and MCM-41) provides a better substrate due to the lack of surface oxide vacancies (unlike  $\gamma\text{-Al}_2\text{O}_3$ ), and consequently there are more four-coordinated  $\text{Ag}^+$  (which can bond olefin) and less five- and six-coordinated  $\text{Ag}^+$  (which cannot bond olefin for steric reason). Anion effects were studied by monolayer  $\text{AgX/SiO}_2$  ( $\text{X}$  = halide), and the bond energies follow the order:  $\text{AgI} > \text{AgBr} > \text{AgCl} > \text{AgF}$ . This result is because the  $d\text{-}\pi^*$  backdonation (rather than the  $\sigma$ -donation) dominates the bonding between  $\text{Ag}^+$  and olefin.

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**KEYWORDS:** Olefin Separations, Sorbent Synthesis, Adsorption of Ethylene and Propylene.

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Exhibit 2  
S.N. 09/632,891



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**RE: UM File #1544 -Olefin-Paraffin Separations by Pressure Swing Adsorption with Complexation Sorbents (Yang, Padin, Rege) -- United States Patent Application**

Dear Linda:

As we discussed on the telephone today, please prepare, file and prosecute a United States patent application for the captioned University of Michigan invention.

As usual, please work directly with the inventors with regard to the technical aspects of this filing and prosecution.



PERGAMON

## Exhibit 3

S.N. 09/632,891

Chemical Engineering Science 55 (2000) 2607–2616

Chemical  
Engineering ScienceNew sorbents for olefin/paraffin separations by adsorption  
via  $\pi$ -complexation: synthesis and effects of substrates

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## Abstract

New adsorbents for olefin/paraffin separations are synthesized by effective dispersion of  $\text{Ag}^+$  cations on high-surface-area substrates. Two techniques for synthesis are compared: thermal monolayer dispersion and incipient wetness impregnation. The incipient wetness impregnation technique yields the best sorbents that show the highest selectivities, olefin capacities, reversibility and fast rates.  $\text{AgNO}_3$  is dispersed on three substrates ( $\gamma\text{-Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and MCM-41 mesoporous molecular sieve) via incipient wetness impregnation for ethane/ethylene and propane/propylene separations. The surface chemistry of the substrate plays an important role in olefin adsorption. The silica surface (on both silica gel and MCM-41) provides a better substrate due to its lack of Lewis acid sites (unlike  $\gamma\text{-Al}_2\text{O}_3$ ), and consequently the Ag atoms in these sorbents are more capable of forming  $\pi$ -complexation bonds with olefins. ESCA results indicate a transfer of electron density from  $\text{Ag}^+$  to the Lewis acid sites of alumina, hence weakens the  $\pi$ -complexation bonds with olefins. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Olefin separations by  $\pi$ -complexation; Sorbent synthesis; Adsorption of ethylene and propylene by supported  $\text{AgNO}_3$

## 1. Introduction

Olefin/paraffin separations represent a class of most important and also most costly separations in the petrochemical industry. Cryogenic distillation has been used for over 60 years for these separations (Keller, Marcinowski, Verma & Williamson, 1992). They continue to be the most energy-intensive distillations because of the close relative volatilities (Humphrey, Seibert & Koort, 1991). The most important olefin/paraffin separations are for the binary mixture of ethane–ethylene and propane–propylene. A number of alternatives have been investigated (Eldridge, 1993). The most promising alternative is separation based on  $\pi$ -complexation.

Separation via  $\pi$ -complexation is a sub-group of chemical complexation where the mixture is brought into contact with a second phase containing a complexing agent (King, 1987). The advantage of chemical complexation is that the bonds are stronger than those formed by van der Waals forces alone. Therefore, it is possible to achieve high selectivity and high capacity for the com-

ponent to be bound. However, these types of bonds are still sufficiently weak to be broken by using simple engineering operations such as raising the temperature and decreasing the pressure.

Separation of olefin/paraffin mixtures based on  $\pi$ -complexation was proposed as early as 1941 (Gilliland, Bliss & Kip, 1941). Early attempts employed liquid solutions containing silver ( $\text{Ag}^+$ ) or cuprous ( $\text{Cu}^+$ ) ions (Quinn, 1971; Ho, Doyle, Savage & Pruett, 1988; Keller et al., 1992; Blytas, 1992; Eldridge, 1993; Safarik & Eldridge, 1998). These attempts met with limited success. There have also been several studies dealing with gas–solid systems (Gilliland et al., 1941; Long, 1972; Xie & Tang, 1990; Kumar, Golden, White & Rokicki, 1992; Yang & Kikkinides, 1995; Yang & Foldes, 1996; Padin & Yang, 1997; Rege, Padin & Yang, 1998; Padin, Yang & Munson, 1999). While gas–solid operations can be simpler as well as more efficient, particularly by pressure swing adsorption, the list of attempts for developing solid  $\pi$ -complexation sorbents is a short one.  $\text{CuCl}$  salt was considered for olefin/paraffin separations (Gilliland et al., 1941; Gilliland, 1945; Long, 1972). However, it lacked adsorption capacity due to the salt's low surface area ( $> 20 \text{ m}^2/\text{g}$ ). Other attempts on developing solid sorbents for  $\pi$ -complexation included silver salts supported on

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